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DEVELOPING THE REACTION KINETICS FOR A BIODIESEL REACTOR

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Abstract

The aim of this paper was to investigate the kinetics of the biodiesel reaction in order to find out how best to reach 96.5% methyl ester. The purity of the biodiesel product was examined using gas chromatography to the EN14214 FAME standard and real-time optical microscopy was used to observe the reaction. The problem was the reaction doesn't reach completion and the mechanism is not understood. It was observed that droplet size had a major influence on reaction end point and that the reaction was mass-transfer limited. This observation was confirmed by developing a mass-transfer based reaction model using the data from the batch reactor which agreed with results from other researchers. The model predicted better conversion with more mixing intensity. The results show that significant improvements could be made to the conventional FAME process.

Key words: Biodiesel, reactor, reaction, transesterification, theory.

Nomenclature

a	m^2/m^3	Surface area per volume of reaction
C_a	mol/m^3	Concentration of reactant a
C_{ao}	mol/m^3	Initial concentration of reactant a
d	m	Diameter of impeller
D	m	Diameter of tank
H	m	Tank height
K	$(\text{mol}/\text{m}^3)\text{s}^{-1}$	Reaction rate constant
n	s^{-1}	Impeller speed
t	s	Residence time
V	m^3	Volume
X_a		Conversion
ρ_c	kg/m^3	Density of continuous phase
μ	$\text{kg}/\text{m.s}$	Viscosity
σ		Surface tension

1. Introduction

In the EU biodiesel is sold to the EN14214 standard which stipulates 96.5% ester content. Biodiesel below this quality can still be sold but is worth less because it must be blended with higher quality fuels. In the biodiesel reaction initial progress is fast with 85% conversion occurring in the first 5 minutes. The problem is after this where the rate drops to almost nothing making it difficult to reach 96.5%. The transesterification reaction is a cascade reaction where the triglyceride (oil) is stripped of fatty acid chains in stages until only glycerol remains. The result of poor conversion is that mono, di and tri-glycerides will remain in the biodiesel as impurities.

In most industrial biodiesel processes the starting oil is mixed with 20%(vol) methoxide (methanol + NaOH) and mixed for 1 hour at just below the boiling point of

methanol (~60°C) followed by settling and washing. Usually 3.5g of NaOH are used per litre of oil plus any extra needed to neutralise the fatty acids. Using this process it is impossible to reach the standard 96.5% ester content using economical operating conditions. When using low quality oils the reaction process is often altered by adding 80% of the methoxide and reacting for 1 hour, followed by a second reaction with the remaining 20% methoxide, after separation of the glycerol containing layer. This alteration makes it possible to use high fatty acid oils (up to 7%) without an acid pre-stage but sacrifices yield (~75%) because soap emulsifies biodiesel into the glycerol layer. This alteration gives the same ester content and it is still economically impractical to reach the standard 96.5% with this method. Another process is to use acid pre-esterification to convert the fatty acids to biodiesel (Haas, 2005). This process can significantly increase the yield when using high fatty acid oils and is essential with fatty acids >10%. However it does not

significantly increase the ester content of the fuel and it is still economically impractical to reach the standard 96.5% with this method. What's needed is a new understanding of the underlying reaction kinetics so that a more effective process can be developed. This paper uses iterative mass transfer and reactor design equations to model biodiesel conversion in a batch reactor.

2. Experimental

For bubble size measurements during reaction a 2 litre closed glass reactor was used and filmed using a camera-microscope-strobe light setup. Samples taken from the reactor were chilled with ice water and quenched with acidic ion-exchange resin to stop the reaction then centrifuged to remove the glycerol. For experiments where multiple data points were needed whilst ensuring that temperature and mixing conditions remained constant, sealed centrifuge tubes were used in a large culture shaker. Reacted biodiesel samples were washed three times by shake mixing with water in centrifuge tubes followed by centrifugation to separate. Gas chromatography was used to measure ester content following the EN14214 method using methylheptadecanoate internal standard (European Committee for Standardization, 2003).

3. Results and discussion

3.1. Proofing the mass transfer mechanism

In order to improve the reaction conversion we must first understand the governing dynamics of the biodiesel reaction. From the thermodynamic calculations it is clear that thermodynamics do not limit the reaction. Therefore there must be a kinetic rate or mass transfer limitation.

Darnoko, Boocock, Freedman, Nouredini and Olivera have all noticed a limiting of conversion at about 85% ester content, where the reaction rate decreases quickly to almost nothing. The problem is that no single reaction mechanism has explained the sudden change in reaction rate and there is substantial disagreement in the literature over its cause. First or second order reaction models don't explain why the reaction stops.

Early experiments involved using both ethanol as well as methanol for the alcohol reactant. Ethylester is the product of reaction involving ethanol and oil just like methylester is the product of reaction involving methanol and oil. An interesting observation was that the ratio of ethyl to methyl ester was equal to the ratio of concentrations of ethanol to methanol used in the reactions. This would only be the case if the reaction was mass transfer limited. If the reaction were kinetic limited the product ratio would correlate to the relative

rates of reaction of methanol and ethanol with oil. Therefore these results indicate that the reaction is for the most part mass transfer limited; however, it does not explain what causes the sudden level out in conversion. There could still be a change in mechanism as suggested by Nouredini and Zhu (1997) which wouldn't be shown on this graph.

Since the reaction is at some point mass transfer limited the next step was to look more closely at droplet sizes through out the reaction. This is difficult work as the droplets are very small and diffract light well. However using the technique of real-time optical microscopy it was possible, at lower impeller speeds, to measure droplet size vs. time in several reactions. The results show the droplet size initially reducing and then increasing.

Only one other author has taken this approach (Olivera *et al.*, 2007) but they used lower temperatures in order to make the droplets visible to the technique via increased viscosity. They reported a reduction of droplet size but noticed no subsequent increase in size because they were not using actual reaction conditions. Evaporation is an important factor because most biodiesel manufacturers operate open non pressurised reactors.

In the reaction soap, mono and di-glycerides are formed which are very surface active, these would reduce interfacial tension so it makes sense that the droplet size would reduce as these intermediates are created. It also makes sense that the droplet size would increase again as they are consumed or trapped inside viscous glycerol droplets. Other droplet size results showed that droplet size was highly sensitive to methanol concentration. Droplet size seemed to increase with decreasing methanol concentration and decrease with added methanol. This was probably because of viscosity variation. Because the reaction takes a long time and is at near methanol boiling point, it is likely that some methanol will evaporate which would therefore reduce droplet size during reaction. It was realised that this size variation could be pivotal to explaining the slow-fast-slow nature of the biodiesel reaction, and why it does not reach completion. The next step was to incorporate this mass transfer limitation into a kinetic model which could be used to make predictions that could be tested.

3.2. Finding order of reaction and rate constants

The real time droplet size data was used to calculate surface area and plotted against the real time ester content to derive the reaction kinetics order of reaction. The reaction rate equation can be modified for mass transfer limited reaction by including an area term. In reality the rate would be dependant on both methanol and oil concentration, but to make the maths solvable we have to base the rate equation on one concentration and include a fudge factor to

compensate. The reaction is in between assumptions of large excess or stoichiometric so a fudge factor of 2 is required to be included in the original concentration term C_{a0} (table 1).

$$X_a = \left(1 - \left(\frac{1}{1 + (k \times at \times C_{a0})} \right) \right)$$

Equation 1 Modified conversion of second order reaction in a batch reactor to include changing interfacial area term.

Terms included are: conversion X_a , rate constant k , interfacial area a , residence time t , and initial concentration C_{a0} .

Curve fitting was used to determine the reaction order by seeing which hypothesis best fit the data points. Figure 1 shows a reaction rate vs. time plot with real data points set against different order of reaction predictions. Real time droplet size data was used in some of the lines to see if that helped the fit. A trial and error method was used to find the rate constant for the curves to match the data points as closely as possible. The hypothesis which fit the closest and was solvable was second order with changing interfacial area during reaction. The two theory lines which do not involve drop size were clearly the worst fit to the real data which is further proof that mass transfer is pivotal to the reaction mechanism.

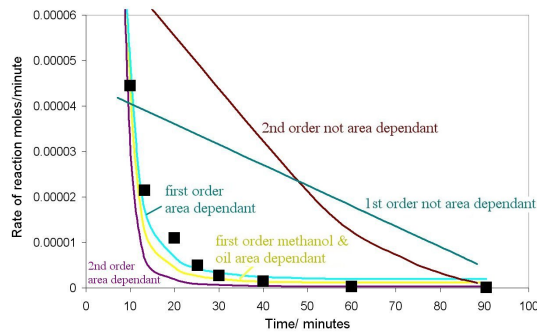


Figure 1 Curve fitting of different reaction rate hypotheses to reaction rate vs time data. Showing that area dependant 2nd order is best fit to experimental data. Reaction conditions 55°C, 6:1 mole ratio, 200rpm.

3.3. Modelling reaction conversion

To model the reaction, we must use a reactor design equation and know the interfacial-area (a) for the system of interest. Interfacial-area depends on droplet size which depends on interfacial tension which changes through out the reaction as components are formed and lost. To find how the degree of conversion effects the interfacial tension during reaction Misek's equation of droplet size was used, first mentioned in Ma *et al*, 1999. This equation was used to calculate interfacial tension from the measured

droplet sizes through out reaction. This interfacial tension was plotted against the conversion to develop an empirical function which could be used for prediction of interfacial tension under different reaction conditions. Table 1 shows the empirical function developed for interfacial tension based on conversion. This was developed using trial and error comparing to data points and quadratic function was the simplest function that best fit the results.

Because of the changing interfacial tension observed it is necessary to relate interfacial tension to conversion and use an iterative formula when trying to model the conversion. To model biodiesel conversion the modified second order batch reactor design equation (equation 1) can be used to calculate conversion. An area term is included to reflect the changing interfacial-area, which is mass transfer limiting. Misek's equation can be used to find this area and the empirical equation for σ (in table 1) can be used to estimate interfacial tension used in the Misek equation. The result of adding these formulae together is the equation shown in equation 2 which can be used to predict biodiesel conversion in reactions.

The conversion used in the empirical equation for σ (table 1) is always taken from the previous time step, therefore making equation 2 iterative. At each time step the product of interfacial-area and time ($a.t$ from equation 1) is calculated by summing the interfacial areas of all previous time steps (using Simons rule) hence the sigma sign in equation 2.

$$X_a = 1 - \left(\frac{1}{1 + KC_{a0} \times \sum \left[(V_{meth} \times 3) / \left(\frac{V_{reactor} \times 1000}{2 \times 10} \times \left(\frac{16.3(H/D)^{0.46} e^{(0.087D)}}{n^2 d^2 \rho_c} \right) \sigma \right) \right]} \right)$$

Equation 2

Table 1

Fit parameters	Value used
K	0.3
σ	$0.0000001c_a^2 - 0.00001c_a + 0.0003$
C_{a0}	$2C_{a0}$

Parameters used to fit equation model to data. K value was arrived upon from figure 1 and visual least squares method, σ

Figure 2 shows the resulting theory lines calculated using this method and shows other methods that are less successful (i.e. assuming first order or not accounting for interfacial-area change). The second order theory that accounts for changing interfacial tension based on conversion is the best fit to the real data and provides the correct slow-fast-slow curve for conversion.

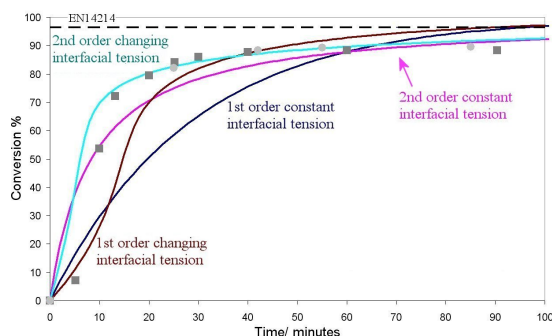


Figure 2 Ester content vs. time graph showing goodness of fit to reaction rate hypotheses. Showing 2nd order changing interfacial tension is the best fit to experimental data. Reaction conditions 55°C, 6:1 mole ratio, 200rpm.

One point worth noting is that the reaction is simplified to the form (oil) \rightarrow (ester) and as such does not show mono and di-glycerides concentration which is negligible most of the time (Boocock *et al*, 1996). One time where these concentrations may not be negligible is at the beginning of the reaction where the theory line shows a sharper increase than the real data points. This may be because the reaction has to first produce mono and di-glycerides to lower the interfacial-tension and boost reaction where as the theory assumes that conversion is straight to ester.

This model is not absolutely accurate, there are ways to improve upon it, but it is a good theory for how a better model could be developed. The model has an R^2 value of 0.79 due to discrepancies with the first data point. Also the results themselves could be inaccurate because gas chromatography is only accurate to within about 5%. The fit parameter in table 1, although many, were needed and sensible. The model could be improved if it was made to be first order in methanol and oil but still second order overall. This would put the maths beyond this authors ability but would remove the need for the $2C_{a0}$ fit parameter. The goodness of fit could also be improved by a better droplet size expression than Misk's equation or a more accurate surface tension vs conversion correlation. The model is good at predicting the end result of the reaction.

This method shows that the reaction is always, both mass transfer limited and rate limited, and that there is no need to split the data into different zones which have different theories. This is a first which no-one else has observed. This theory can now be used to show how conversion depends on the reaction variables such as mixing and to predict how new reactor designs will behave.

3.5. Effect of temperature

Now Arrhenius' equation can be used to calculate the dependence of rate upon temperature and make predictions of reaction rate at higher temperatures.

Using Nouredini and Zhu's data (1997) for conversion vs time at different temperatures a graph can be drawn of $\ln(k)$ vs. $1/T$ which exhibits a straight line. The gradient of this straight line is equal to $-E/R$ where R is the ideal gas constant. Once the constants k_0 and E have been calculated rate constants at different temperatures can be calculated. For the mass transfer limited second order theory Figure 3 shows how these new rate constants work at the different temperatures used in the Nouredini data. Nouredini himself noted that "the effects of temperature look a lot like the effects of impeller speed" this is because the terms that are affected are in the same place in the overall rate equation.

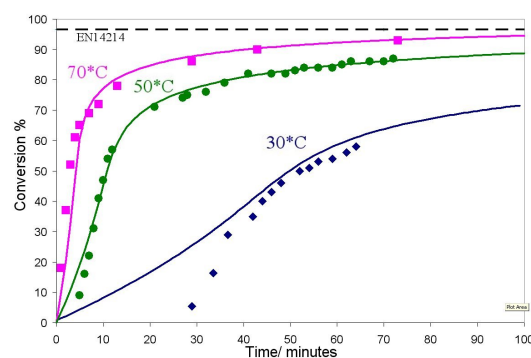


Figure 3 Reaction conversion vs. time curves at different temperatures. Reaction conditions 6:1 mole ratio, 3100Re. Original theory lines plotted against data points taken from Nouredini (1997).

Temperature affects viscosity which would affect Reynolds number but this is not taken into account in the Misk equation for droplet size. Therefore there could be deviations from this theory that could be solved by using a better equation for droplet size which includes a viscosity term. However the theory clearly holds up even without this. The initial difference between theory and data points for the 30°C data maybe due to mono and di-glyceride formation and settling. Often at insufficient impeller speeds or poor vessel configurations the methanol reactant can stay floating on top of the oil and the impeller will only suck down a few droplets at a time until the reaction has progressed to the extent that the viscosity and interfacial tension is lowered enough to fully disperse the methanol reactant. This has the effect of artificially delaying the start of reaction.

4. Conclusion

The biodiesel reaction was studied using optical microscopy to measure droplet size during reaction. The droplet size was observed to initially decrease and then increase which correlated with the creation of surface active intermediary's and then the consumption and evaporation of methanol. This observation was seen to explain the slow-fast-slow nature which limits the biodiesel reaction. For the first time both mass transfer and reaction rate were shown to be limiting conversion throughout the reaction. For the first time a numerical theory was developed which fitted the data. This is a flexible model and ways are mentioned of how to change for different situations or improve the model.

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